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DIBENZYL STRUCTURES IN A MACROMOLECULAR CHAIN. III. DIBENZYLDIISOCYANATES REACTIVITY†

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ABSTRACT

The reactivity of the 2,2′-, 2,4′-, 4,4′-dibenzyldiisocyanate (2,2′-, 2,4′-, 4,4′-DBDI) with *n*-butanol in benzene has been studied. The concentrations of all species were monitored by using high performance liquid chromatography (HPLC). The reactivity of 4,4′-DBDI is similar to that of 4,4′-diphenylmethanediisocyanate (4,4′-MDI). Very strong intramolecular catalytic effects were noticed in the case of 2,2′-DBDI, probably due to the variable molecular geometry. These effects are responsible for the whole reaction pattern. The 2,4′-DBDI NCO *ortho* and *para* groups reactivities are different and comparable to that of 2,4-toluylenediisocyanate (2,4-TDI).

INTRODUCTION

In previous papers [1], a series of polymers based on dibenzylic monomers were presented. These monomers belong to a large category of

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†For Part II, see G. Caraculacu, A. Caraculacu, E. Scortanu, Cr. Luchian, T. Buruiana, and I. Agherghinei, *Mater. Plast.*, *23*(4), 187–191 (1986).

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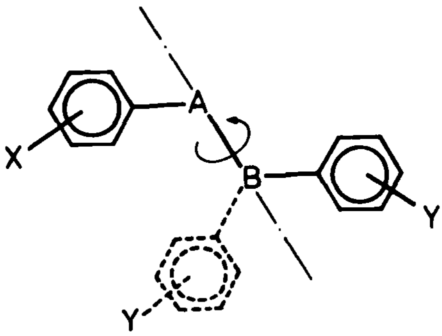
diaromatic compounds with variable geometry. This may be due to rotation around the A–B bridge as shown by



(1)

where X and Y = functional groups, and A and B = $-CH_2-$, $-CR_1R_2-$, $-CO-$, $-NH-$, $-NR-$, $-S-$, $-SO-$, and $-SO_2-$.

It was established [1] that the presence of the dibenzylic structure induces significant effects in macromolecular chains, especially those connected to the rearranging capacity of the molecular fragments and thus to the increase in the degree of crystallinity. During the synthesis of urethanic polymers through homogeneous polyaddition, disproportionation accompanies the reaction, leading to the simultaneous synthesis of polyurethanes with different relative ratios of the components in both solution and suspension media.

In order to clarify the mechanism of this process, the dibenzyldiisocyanates reactivities were studied.

This paper deals with an investigation of the reaction kinetics of 2,2′-, 2,4′-, and 4,4′-DBDI with *n*-butanol (BuOH). The previously presented technique [2, 3] permitted us to follow the concentration values for all molecular species by using the HPLC method.

As in our former work, the NCO/OH group ratio has a value of 2 as it has in the case of polyurethane prepolymer synthesis conditions. Benzene was selected as the reaction solvent because of its low polarity, thus permitting us to monitor the catalytic effects of the alcohol and the resulting urethanes. The effect of various functional groups and solvents on polyaddition processes has also been studied, e.g., the influence of alcohol concentration, the addition of urethane, ester, and ether groups, and polar solvents.

By using monofunctional model compounds and IR and cryoscopic

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techniques, the association processes of various reaction pairs were analyzed.

EXPERIMENTAL

Materials

2,2′-, 2,4′-, and 4,4′-DBDI monomers were vacuum distilled. The NCO content of the starting materials and their isomeric purity were established by chemical methods [4] and HPLC.

Benzene, cyclohexane, petroleum ether, and *n*-hexane were dried with sodium and distilled before use. P.a. grade butyl and methyl alcohol were purified as described in a previous paper [2].

IR (KBr pellets) measurements were carried out on a Perkin-Elmer 577 Spectrophotometer. ^{1}H-NMR measurements were performed with the aid of a 60-MHz Jeol instrument. A UV variable-wavelength 1030 B Detector, Hewlett-Packard 1084 Chromatograph was selected for the HPLC measurements.

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Model Synthesis

Seven new model HPLC standard compounds were synthesized with the following structure:

$$R_1-O-CO-NH-R_2-NH-CO-O-R_3$$

See Table 1.

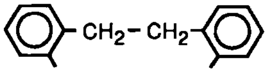
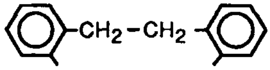
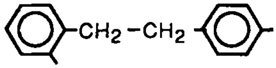
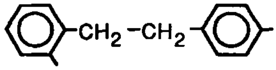
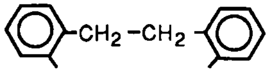
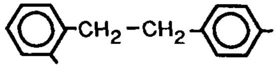
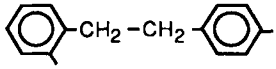
The symmetrically disubstituted models were synthesized according to previously published methods [2, 3]. The reaction yields for the raw materials were quantitative. The nature of the recrystallization solvents, the corresponding melting points, and the elemental analysis data are presented in Table 2.

The asymmetrically disubstituted models (1e–1f) were synthesized under anhydrous conditions by the following set of reactions.

1,2-Ethylene bis(o-carbanilic acid)methyl, n-butyl ester (1e)

To 5.42 g of freshly distilled 2,2′-DBDI dissolved in 50 mL anhydrous DMF, 2 mL anhydrous *n*-butanol was added. The mixture was then heated at 60°C for 10 h. The DMF was then removed through vacuum distil-

TABLE 1. Models for HPLC

No.	R_1	R_2	R_3
1a	CH_3		CH_3
b	C_4H_9		C_4H_9
c	CH_3		CH_3
d	C_4H_9		C_4H_9
e	CH_3		C_4H_9
f	CH_3		C_4H_9
g	C_4H_9		CH_3

lation (0.8 mmHg), and the residue was mixed with 32 mL anhydrous benzene. The resulting solution was cooled by using an ice bath and then filtered. The resulting crystals were recrystallized from 90 mL cyclohexane at −15°C. Methanol (50 mL) was added to the product obtained, and the system was kept at 60°C overnight. The solvent was removed through evaporation, and the 3.36 g residue was extracted with 35 mL methanol and filtered. Water (15 mL) was added to the solution, followed by heating and crystallization. The resulting 2 g of crystalline material was recrystallized from 170 mL of a 2:1 methanol:water mixture and then redissolved in an identical 135 mL methanol:water mixture while heating. After cooling and filtering, the clear solution was reduced to 1/4 of its volume by solvent evaporation. After cooling and filtering, crystals (0.3 g) were separated. In addition, two recrystallizations were continuously performed by using 20 and 14 mL 2:1 methanol:water mixtures, respectively. A model compound (0.15 g, mp 114.5–115°C) (1e) eventual-

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TABLE 2. HPLC Models

No.	Model	Recrystallization Solvent	Recrystallization No.	mp, °C	Formula	Molecular weight	Elemental analysis C, % calc (found)	Elemental analysis H, % calc (found)	Elemental analysis N, % calc (found)
a. Models with the Same Substituent at Urethane Groups									
1a.	1,2-Ethylene bis(*o*-carbanilic acid)dimethyl ester	MeOH	4	172	$C_{18}H_{20}N_2O_4$	329.4	65.85 (65.67)	6.10 (6.08)	8.54 (9.10)
1b.	1,2-Ethylene bis(*o*-carbanilic acid)di-*n*-butylester	DMF:water, 5:1 MeOH	3 1	138–139	$C_{24}H_{32}N_2O_4$	412.5	69.90 (70.49)	7.77 (7.57)	6.80 (6.50)
1c.	1,2-Ethylene *o*-carbanilic acid methyl, *p*-carbanilic acid methyl diester	MeOH	4	139.5–142	$C_{18}H_{20}N_2O_4$	329.4	65.85 (65.77)	6.10 (6.11)	8.54 (8.45)
1d.	1,2-Ethylene *o*-carbanilic acid butyl, *p*-carbanilic acid butyl diester	MeOH	4	83.5–85	$C_{24}H_{32}N_2O_4$	412.5	69.90 (70.05)	7.77 (7.66)	6.80 (5.77)
b. Models with Different Substituents at Urethane Groups									
1e.	1,2-Ethylene bis(*o*-carbanilic acid) methyl, *n*-butyl ester			114.5–115	$C_{21}H_{26}N_2O_4$	370.4	68.09 (67.93)	7.07 (6.85)	7.56 (7.23)
1f.	1,2-Ethylene, *o*-carbanilic acid methyl, *p*-carbanilic acid *n*-butyl diester			117–118	$C_{21}H_{26}N_2O_4$	370.4	68.09 (68.31)	7.07 (6.88)	7.56 (7.28)
1g.	1,2-Ethylene *o*-carbanilic acid *n*-butyl, *p*-carbanilic acid methyl diester			102–105	$C_{21}H_{26}N_2O_4$	370.4	68.09 (67.94)	7.07 (6.99)	7.56 (8.03)

ly resulted. The structure and purity of the final compound were established by means of ^{1}H NMR, elemental analysis, and HPLC (Table 2).

1,2-Ethylene, o-carbanilic acid methyl, p-carbanilic acid n-butyl, diester (1f)

An anhydrous *n*-butanol mixture (2.31 g) containing one drop of anhydrous pyridine was added to a mixture of 8.25 g freshly distilled 2,4′-DBDI and 13 mL anhydrous cyclohexane and stirred for 20 min. The reaction mixture was stirred continuously at room temperature for 5 h (until a homogeneous solution formed), then 10 mL anhydrous petroleum ether was added. The resulting crystalline material was separated and washed with anhydrous petroleum ether. Monoisocyanate (6.6 g) was eventually obtained and was recrystallized from a 60-mL 1:1 anhydrous cyclohexane:*n*-heptane solution and from a 200-mL 1:1 cyclohexane: petroleum ether solution. After cooling (−25°C) and filtering, the crystalline material was dried under vacuum. Finally, 3.25 g monoisocyanate (76–77°C mp) was obtained.

The monoisocyanate (2.5 g), dissolved in 20 mL dried benzene, was treated with 10 mL methanol and 0.5 mL anhydrous pyridine, and the solution was kept overnight at 60°C. After removing the solvent, the resulting residue (3.2 g) was recrystallized three times from 3:1 methanol:water and then from a 1:6 methanol:water solution. A model compound (1f) (0.3 g, 117–118°C mp) was eventually obtained. The H-NMR spectra, HPLC, and elemental analysis data proved the structure of the compound (Table 2).

1,2-Ethylene, o-carbanilic acid n-butyl, p-carbanilic acid methyl diester (1g)

A solution of 1 g methanol and a drop of anhydrous pyridine were added to a solution of 8.25 g freshly distilled 2,4-DBDI which was dissolved in 13 mL anhydrous cyclohexane and stirred for 20 min. Two layers of nonmiscible liquids appeared during the reaction and turned into a crystalline suspension after 2 h. The stirring was maintained for 6 or more hours. The resulting solid was washed twice after filtration with 20 mL anhydrous cyclohexane, then washed twice with 20 mL anhydrous petroleum ether. The mixture was extracted in the next phase with 250 mL anhydrous *n*-hexane. The cooled solution was stirred overnight. After filtration, the crystalline compound was washed with petroleum ether

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and anhydrous benzene, followed by vacuum drying. The resulting 5 g of monoisocyanate was dissolved in 20 mL dried benzene, treated with 10 mL anhydrous *n*-butanol and 0.5 mL anhydrous pyridine, and then kept overnight. The solvent was removed by evaporation. The residue was recrystallized from a 3:1 methanol:water mixture and then from a 1:3 methanol:water mixture. One gram of the model compound (1g) (102–105°C mp) was obtained. Its structure was proven by ^{1}H-NMR spectra, HPLC, and elemental analysis data (Table 2).

Kinetics Measurements

Kinetic measurements were carried out at 60°C according to a method previously presented [2]. For most cases, the starting molar concentrations of diisocyanates were equal to that of the *n*-butanol (0.175 mol/L).

Benzene was not used in the preparation of *n*-butanol solutions when the influences of butyl acetate, di-*n*-butyl ether, and DMF were estimated. Benzene was used, however, for preparing the diisocyanate solutions.

In order to monitor the influence of alcohol on the kinetics [in the case of kinetic reaction 10 (Table 4)], *n*-butanol was replaced by methanol. The reaction was stopped by using *n*-butanol, thus permitting the use of the same HPLC standard as in the case of the initial procedure (kinetic reaction 6, Table 4). *HPLC analyses* were carried out under conditions described in previous papers [2, 3]. The modified experimental conditions for 2,2′-DBDI and 2,4′-DBDI, in comparison to 4,4′-DBDI, are presented in Table 3.

It is worthy to mention that the individual compounds were completely separated from one another.

Cryoscopic measurements were performed in benzene in anhydrous conditions by using a Beckman-type apparatus (0.01°C sensibility thermometer) provided with an outside vertically actioned magnetic stirrer. In the first step, the freezing points of anhydrous benzene and of only one compound solution (0.35 mol/L) were recorded. In the second step, the freezing points of equal volume mixtures of the above solutions were measured.

The corresponding mixtures were prepared directly in the cryoscopic instrument. The working procedure and estimation of the molecular weights followed the standard procedure [5].

IR measurements were performed on both the cryoscopic solutions and the corresponding mixtures by using a Perkin-Elmer 577 spectrophotometer and 0.2 mm KBr cells with anhydrous benzene as the reference.

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TABLE 3. HPLC Chromatographic Conditions

Diisocyanate	Time, min	Mobile phase Water, 80°C, vol%	 Methanol, 40°C vol%	Flow, mL/min	Wavelength, nm	Retention time Species[a]	 Model	 min
2,2′-DBDI		20	80	1	232	n′	1a	3.78
						m′	1e	6.05
						b	1b	11.85
		Gradient						
2,4′-DBDI	11	32	68	1	240	n′	1c	5.14
	4	32	68			m_1'	1g	10.56
	8	20	80			m_2'	1f	11.71
		20	80			b	1d	20.25

[a] n′ = unreacted diisocyanates (blocked as 1a or 1c). m′, m_1', m_2' = monoreacted diisocyanates (blocked as 1e, 1g, or 1f). b = bireacted diisocyanates (1b or 1d).

RESULTS AND DISCUSSION

The $F_{Nexp}\%$ (F_N = molar fraction of unreacted diisocyanate) dependence versus the reduced time τ was determined according to methods presented in another paper [2] (Fig. 1).

Due to the change in the rate constants during the reaction, both the initial and average rate-constant values were calculated.

The rate constants of the initial and average stages of the process and the values of the rate-constant ratios are presented in Table 4. These values correspond to the reactions of the first and second NCO groups of the symmetrical DBDI isocyanates (2,2′ and 4,4′) and to those of the 4,4′-diphenylmethanediisocyanate reaction. Note that the reactivity values of 4,4′-DBDI are very close to those of 4,4′-MDI, and these values barely change during the reactions.

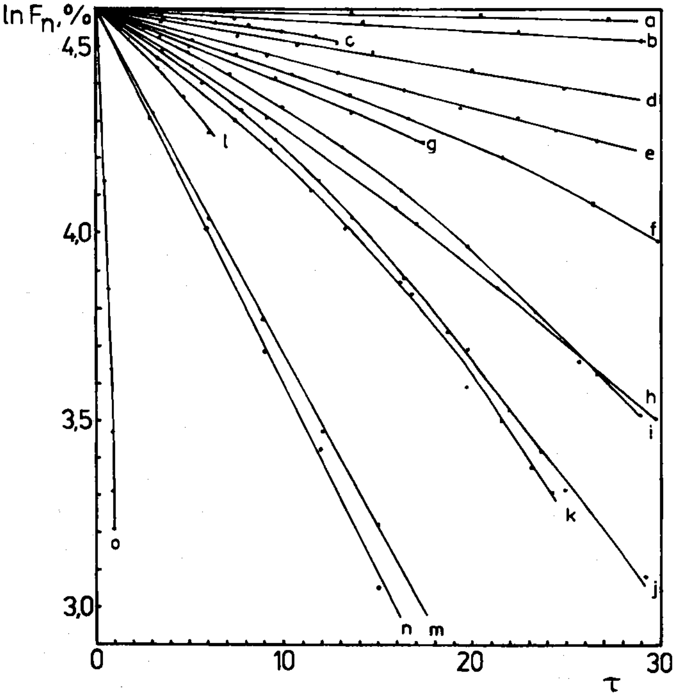

FIG. 1. Dependence of the ln F_N (%) function on τ. Number of kinetic runs: a = 10, b = 6, c = 4, d = 12, e = 7, f = 14, g = 3, h = 15, i = 11, j = 1, k = 2, l = 5, m = 9, n = 8, o = 13.

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TABLE 4. Results of Kinetic Measurements on the Reaction between Symmetrical Diisocyanates and *n*-Butanol in Benzene ($mol^{-1} \cdot min^{-1} \cdot L$) at 60°C

Number of kinetic reaction[h]	Diisocyanate type	Concentration mol/L	$10^2 \times k_1$ (determined)		$R = k_1/k_2$ (determined)	$10^2 \times k_2 = k_1/R$ (calculated)	
			Initial	Average		Initial	Average
1	4,4′-DBDI	0.175	1.81	2.10	1.3	1.39	1.61
2	4,4′-MDI	0.175	2.13	2.28	1.36	1.57	1.68
3	4,4′-DBDI	0.0875	1.02	1.02	1.3	0.785	0.785
4	4,4′-DBDI	0.035	0.329	–	[g]	–	–
5[a]	4,4′-DBDI	0.035	2.58	2.58	1.0	2.58	2.58
6	2,2′-DBDI	0.175	0.14	0.147	0.0035[e]	[f]	–
7[b]	2,2′-DBDI	0.175	0.688	0.674	–	[f]	–
8	2,2′-DBDI	0.035	5.07	5.07	0.126	40.2	40.2
9[c]	2,2′-DBDI	0.035	4.67	4.67	0.123	38.0	38.0
10[d]	2,2′DBDI	0.175	0.0499	0.0594	–	[f]	–

[a] With addition of 1,2-ethylene bis(*p*-carbanilic acid dibutyl ester) (concentration = 0.04375 mol/L).

[b] With addition of carbanilic acid methyl ester (concentration = 0.35 mol/L).

[c] With addition of carbanilic acid methyl ester (concentration = 0.075 mol/L).

[d] Reaction with MeOH instead of *n*-butanol; quenching with *n*-butanol.

[e] Calculated from k_1/k_2 value, where k_2 was adopted as equal to that found in kinetic reaction 8.

[f] Measurable quantities of monoreacted isocyanate are not detectable by the HPLC method.

[g] The reaction was performed only to low conversions (up to 10%) which did not allow the R calculation.

[h] For all kinetic reactions, the NCO/OH ratio is 2 except for kinetic reactions 8 and 9 where the value is 0.01282.

Reactions 1, 3, and 4 were carried out under similar experimental conditions. The only parameter which differed in these reactions was the concentration of the solutions.

The k_l versus concentration dependence (Fig. 2) is linear, which permits the estimation of an F factor value of 0.1.

$$F = k_l/C_{4,4'\text{-DBDI}} = 0.01/0.095 = 0.1$$

Reactions 6, 7, and 10, in the case of 2,2′-DBDI, represent an unexpected result. At the end of the reaction, a mixture containing equal amounts of unreacted 2,2′-DBDI and the diurethane n derivative were obtained (Fig. 3).

In order to understand this phenomenon, two hypotheses were considered:

1. Stabilization of neighboring NCO groups resulting from the pairing of 2,2′-DBDI dipoles, which leads to the formation of a system with lower energy (Eq. a). By destroying this system after a collision with a

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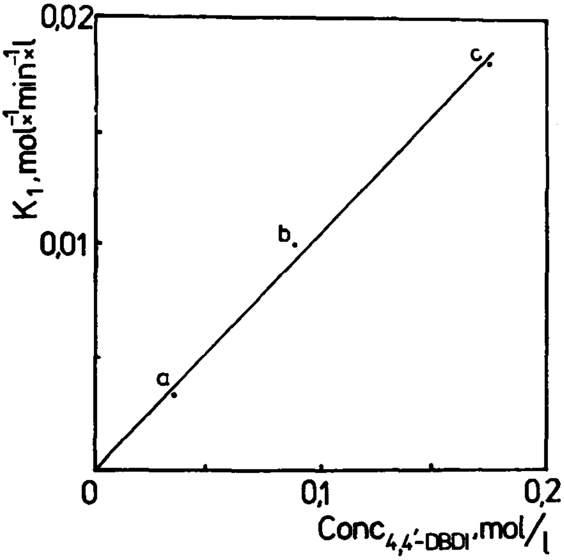

FIG. 2. k_1 variation versus reactant concentration in the reaction of 4,4′-DBDI with n-butanol; NCO/OH = 1; 60°C in benzene. Number of kinetic runs: a = 4, b = 3, c = 1.

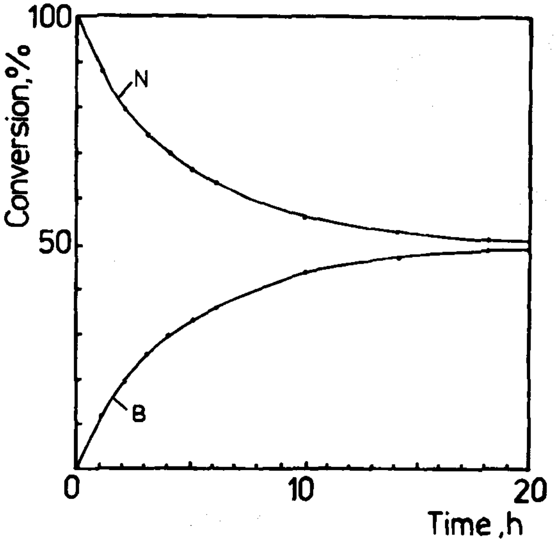

FIG. 3. Composition variation in the reaction of 2,2'-DBDI with *n*-butanol; NCO/OH = 2 (kinetic 6), N = unreacted 2,2'-DBDI, B = bireacted 2,2'-DBDI

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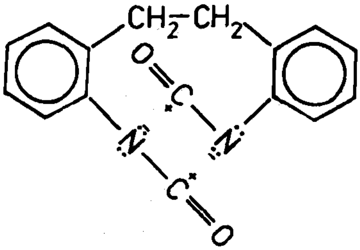
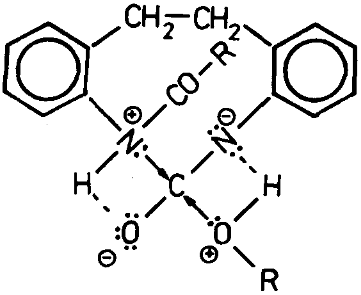
higher energy alcohol molecule, the reaction should take place simultaneously at both NCO groups.



(*a*)

2. A very strong acceleration of the second stage of the reaction between 2,2'-DBDI and alcohol. This might be due to the catalytic effect of the neighboring urethane group which was formed in the first stage as a result of the reaction of one of the NCO groups.



(*b*)

In order to verify the possibility of association between various groups of the systems, model compounds were used and a cryoscopic method was adopted. Benzene was selected as the solvent; the concentration was 0.35 mol/L. In the case of mixtures, similar molar concentrations were selected as those used in kinetic measurements (0.175 mol/L).

The freezing points of pure benzene solutions of the compounds and of their binary mixtures were monitored. Tables 5 and 7 exhibit the cryoscopic results.

Significant associations in benzene were noticed only in the cases of alcoholic and urethanic groups. IR measurements also exhibit peculiar absorptions for hydrogen bonding (3460 and 3320 cm^{-1}).

IR and cryoscopic analyses do not prove associations between the NCO groups (Table 5). These findings call into question the existence of type *a* complexes.

Regarding the second hypothesis, in order to estimate the catalytic effect of the urethane groups, comparative kinetic measurements were carried out by introducing urethanes in the reaction medium (reactions 6 and 7, Table 4) and maintaining identical experimental conditions.

It should be noted that an initial urethane/NCO ratio of 1/1 (reaction 7) gives a significant increase of the reaction rate. The 4.6-fold increase of the rate constant indicates the accuracy of the second hypothesis.

Additional evidence was recorded by performing kinetic measurements using excess alcohol (reactions 8 and 9, Table 4), thereby decreasing the urethane group influence on the catalytic effects in comparison to that of the higher number of OH groups. In this case, HPLC data clearly show the temporary appearance of a monoreacted product, which certainly is consumed during the development of the reaction (Fig. 4). Thus, the kinetic data allowed us to estimate the rate constants for both the first and second steps of the reaction.

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TABLE 5. Cryoscopic Measurements for Individual Compounds at Concentrations of 0.35 mol/L in Anhydrous Benzene[a]

No.	Substance	G_B	ΔT	M_e	M_t	M_e/M_t
1	Phenylisocyanate (FI)	50.1	2.1645	117	119	1
2	*n*-Butanol	30.74	1.42	110	74.12	1.48
3	Carbanilic acid methyl ester (FMU)	63.23	1.67	192	151	1.27
4	Butylacetate (BuAc)	48.72	2.25	110	116	1
5	Di-*n*-butylether (DBE)	55.52	2.25	125	130.22	1
6	Dimethylformamide (DMF)	30.08	2.04	75	73	1

[a] M_e = experimental molecular mass. M_t = theoretically molecular mass. G_B = grams of dissolved substance in 1000 g benzene. ΔT = difference between freezing temperature of benzene and of solution. $M_e = 5.07 G_B/\Delta T$.

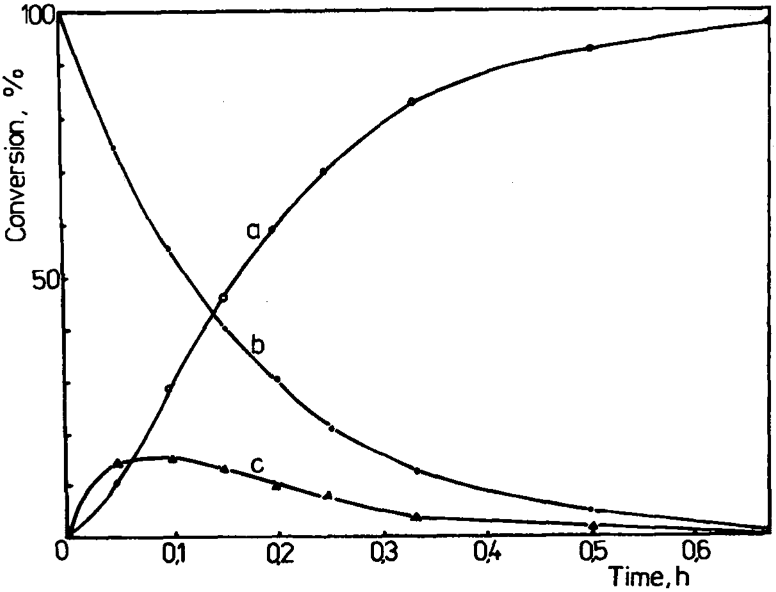

FIG. 4. Composition variation in the reaction of 2,2′-DBDI with *n*-butanol in excess; NCO/OH = 0.01282 (kinetic 8), a = bireacted 2,2′-DBDI, b = unreacted 2,2′-DBDI, c = monoreacted 2,2′-DBDI.

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As observed from reaction 9, initial additions of urethane groups have a negligible catalytic effect in comparison to that of the numerous OH groups. The presence of the OH group excess mainly influences the first reaction by bringing its rate to comparable values with that of the second reaction. A $R_1/R_2 = 0.126$ ratio was recorded, suggesting that the steric displacement of the urethane groups (structure *b*), appearing in the first step, exhibit higher catalytic effects than that of the OH groups. This is the case even though the latter are 78 times more numerous then the initial NCO groups.

Additional evidence can be presented for the second hypothesis if the rate constant for the reaction of 2,2′-DBDI ($k_1 = 1.4 \times 10^{-3}$, reaction 6, Table 4) is compared under similar conditions to the rate constant of the reaction of 2,4′-DBDI ($k = 1.59 \times 10^{-3}$, reaction 14, Table 8). It should be noted that both reactions have nearly the same rate-constant values. Consequently, it is suggested that in the case of 2,2′-DBDI, the first reaction is followed by a strong acceleration of the second reaction.

In the case of reaction 8, the catalytic effect of the excess alcohol does not increase the reaction rate of the second NCO group, so the k_2 constant can be adopted from reaction 6. In this case a $k_1/k_2 = 0.0036$ ratio results, which indicates that in the second step the reaction should increase 286 times, and for this reason the monoreacted species could not be tracked in the case of kinetic reaction 6.

The rate modifications were also followed through the steric effects produced by replacing *n*-butanol with methanol. By comparing reactions 10 and 6 (Table 4), it can be observed that, contrary to expectation, the average rate constant decreases by a factor of 2.47. A similar decrease was also observed in the case of the reaction between phenyl isocyanate and alcohols by merely changing from ethyl to methyl; the ratio is $(0.51 \times 10^{-2})/(0.29 \times 10^{-2}) = 1.76$ [6]. This behavior was explained by the authors as the predominant polar effect of the OH group relative to its steric effect.

The effects of various functional groups and some polar aprotic solvents (for instance, DMF) on the kinetics are presented in Table 6.

Note that the presence of DBE and BuAc gave a 1.46- and a 4.4-fold decrease in reaction rates, respectively, in comparison with reaction 1 (Table 4). This observation has been made by other authors [7, 8].

This behavior was rationalized as being due to modifications in hydrogen bonding by limiting the number of OH groups involved in the formation of a catalytic complex [7]. Additional evidence can be obtained from

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TABLE 6. The Influence of Ester, Ether, and Amide Groups on the Kinetics of the Reaction between 4,4′-DBDI and *n*-Butanol

Number of kinetic reaction	Solvents (volume ratio)	$10^2 \times k_1$ (determined), $mol^{-1} \cdot min^{-1} \cdot L$		$R = k_1/k_2$ (determined)	$10^2 \times k_2 = k_1/R$ (calculated) $mol^{-1} \cdot min^{-1} \cdot L$	
		Initial	Average		Initial	Average
11	Bz–DBE (1:1)	1.17	1.44	1.33	0.9	1.11
12	Bz–BuAc (1:1)	0.474	0.477	1.44	0.329	0.331
13	Bz–DMF (1:1)	58.1	61.5	1.05	55.3	58.6

[a] Bz = benzene, DBE = di-*n*-butyl ester, BuAc = butyl acetate, and DMF = *N,N*-dimethylformamide. Concentration = 0.175 mol/L; NCO/OH = 2; 60°C.

cryoscopic measurements of the intermolecular associations in equimolar model mixtures having NCO, OH, and NH—CO—O groups (Table 7).

The observation that the ratio of $\Delta t_{obs}/\Delta t_{calc} = 1$ for all mixtures (except numbers 1 and 10) suggests the absence of significant associations. IR data also support that the OH groups are not hydrogen bonded (3590 cm^{-1}).

Equimolar mixtures of alcohols and solvents capable of forming hydrogen bondings, such as $R—OH\cdots\cdots O=C(OBu)CH_3$ in BuAc and $R—OH\cdots\cdots O(R)_2$ in DBE, exhibit IR spectra which present only a small shift of the vibrations of dimeric associations. For example, $R—OH\cdots\cdots O(H)R$ shifts from 3460 cm^{-1} in pure benzene to 3545 cm^{-1} (BuAc) and 3480 cm^{-1} (DBE), respectively.

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TABLE 7. The Results of Solution Mixture Cryoscopic Measurements at a Concentration of 0.175 mol/L of Each Component in Anhydrous Benzene

No.	1/1 volume mixture of the components in Table 3	Δt_{obs}, °C	Δt_{calc},[a] °C	$\Delta t_{obs}/\Delta t_{calc}$
1[b]	1 + 2	1.96	1.79	1.09
2	1 + 3	1.98	1.92	1.03
3	2 + 3	1.64	1.54	1.06
4	1 + 4	2.19	2.21	0.99
5	2 + 4	1.81	1.83	0.99
6	1 + 5	2.23	2.21	1.01
7	2 + 5	1.88	1.84	1.02
8	1 + 6	2.13	2.10	1.01
9	2 + 6	1.72	1.73	0.90
10	3 + 6	1.62	1.85	0.87

[a] Δt_{calc} obtained as the average between the Δt_{obs} values (from Table 5) of each component.

[b] Measurements were made immediately after mixing the component parts at about 6–8°C in order to avoid reactions between components. Detected by monitoring the CO of the urethane group in the IR spectra.

The increase in the value of the ratio $\Delta t_{obs}/\Delta t_{calc}$ = 1.09 in the case of FI + BuOH (No. 1, Table 7) suggests a decrease of OH group associations. This is also confirmed by IR spectra which show a decrease of the intensity of dimeric absorption (3460 cm^{-1}) (Fig. 5).

In the case of the FMU + DMF mixture (case on. 10), the $\Delta t_{obs}/\Delta t_{calc}$ = 0.87 value suggests intensified associations, and the IR data are in good agreement with this conclusion (3280 cm^{-1}) (Fig. 6).

It is noteworthy that the BuOh + DMF mixture $\Delta t_{calc}/\Delta t_{obs}$ ratio value (No. 9, Table 7) does not indicate association changes, while the IR spectra exhibit significant intensification of the dimer maximum 3450 cm^{-1} (Fig. 7).

The effect of a higher level of solvent concentration, which corresponds to real-reaction conditions (Table 6), clearly shows from IR data that the balance of unassociated to associated alcohol molecules significantly shifts to the latter. These data are also in good agreement with our rationale for the decrease in the reaction rate for DBE and BuAc.

However, the DMF system represents a special case due to the fact that

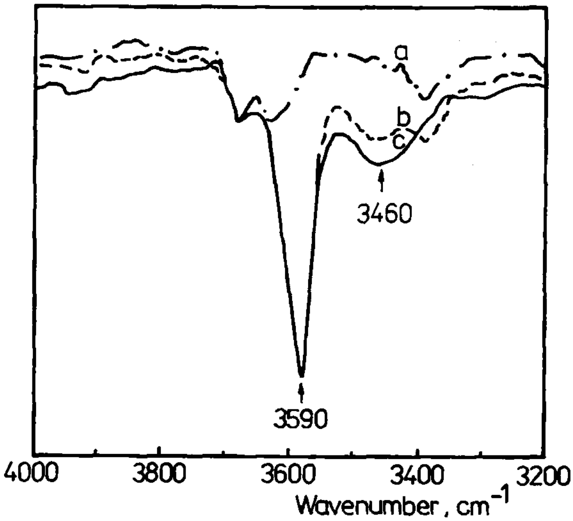

FIG. 5. IR spectra: a = phenyl isocyanate (concentration = 0.175 mol/L); b = mixture of *n*-butanol (concentration = 0.175 mol/L) with phenyl isocyanate (concentration = 0.175 mol/L); c = *n*-butanol (concentration = 0.175 mol/L); solvent, benzene.

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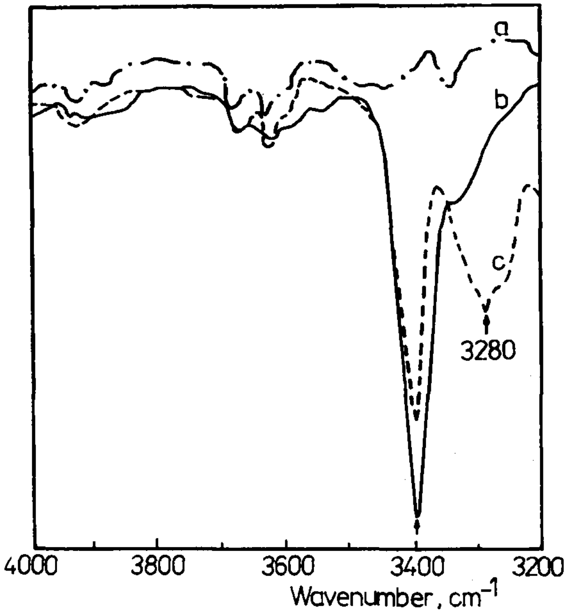

FIG. 6. IR spectra: a = DMF (concentration = 0.175 mol/L); b = FMU (concentration = 0.175 mol/L); c = mixture of DMF (concentration = 0.175 mol/L) with FMU (concentration = 0.175 mol/L); solvent, benzene.

there is a reaction between 4,4′-DBDI and DMF leading to bis(*N*,*N*-dimethyl-*N*′-*p*-benzylformamidine). In boiling DMF, this reaction is practically quantitative within a few hours [9]. Nevertheless, we studied the kinetics in the presence of this solvent because of its general utility for polyurethane synthesis. Since the reaction is performed at lower temperatures and there is a significant difference between OH and DMF reactivities, we showed by HPLC that the DMF/isocyanate reaction represents approximately 1% of the total. Moreover, at room temperature, IR and cryoscopic evidence could not detect any association between DMF and the NCO groups. DMF generates a large catalytic effect which exceeds the expected decrease in the catalytic effect of the alcohol. The overall result is a tenfold increase of the reaction rate constant.

One can conclude that the presence of apparently inert functional groups in these reactions has to be taken into account for reliable kinetic data in polyurethane syntheses which must include polyester and polyether intermediates.

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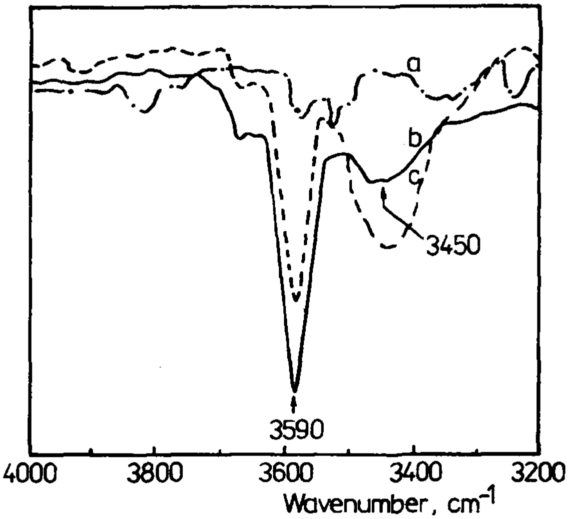

FIG. 7. IR spectra: a = DMF (concentration = 0.175 mol/L); b = *n*-butanol (concentration = 0.175 mol/L); c = mixture of DMF (concentration = 0.175 mol/L) with *n*-butanol (concentration = 0.175 mol/L); solvent, benzene.

The kinetic characterization of the reaction of the asymmetric diisocyanate 2,4′-DBDI was similar to 2,4-TDI [3]. Due to the efficient chromatographic separation of the *ortho* and *para* monoreacted isomers, the reactions could be monitored without difficulty. The concentration variation of the species during the development of the reaction is plotted in Fig. 8.

Table 8 exhibits the kinetic data of 2,4′-DBDI in comparison to that of 2,4-TDI.

Low stability of the final system was noticed in the case of reaction 14 at high conversion, which is similar to 2,4-TDI. The result is probably due to gradual consumption of NCO groups through secondary reactions. Nevertheless, the concentration values at the end of the main reactions (the intersection of the b and c curves, Fig. 8) are in good agreement with the theoretical calculations.

Some of the differences between 2,4′-DBDI and 2,4-TDI should be noted. First the latter is a more active isocyanate than 2,4′-DBDI due to the mutual activation of the NCO groups on the same phenyl ring. The initial reactivity difference between *ortho* and *para* NCO groups was greater for 2,4′-DBDI than that for 2,4-TDI, due probably to the steric

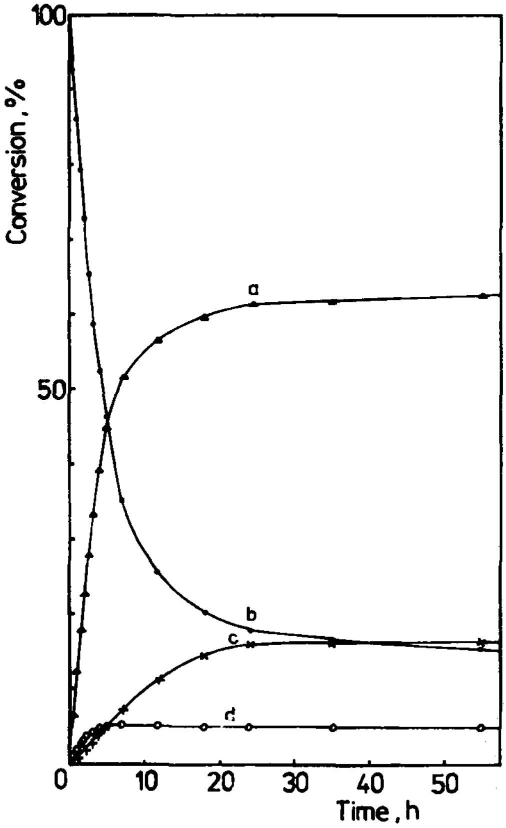

FIG. 8. Composition variation in the reaction of 2,4'-DBDI with *n*-butanol (kinetic 14), a = *para* reacted 2,4'-DBDI, b = unreacted 2,4'-DBDI, c = bi-reacted 2,4'-DBDI, d = *ortho* reacted 2,4'-DBDI.

effect of the *ortho* substituent. The reaction rate of the NCO group in 2,4'-DBDI, belonging to the "Ac" type aromatic diisocyanate [3], was insignificantly modified after the reaction of the first NCO group. The k_1/k_1' and k_2k_2' ratios were approximately 1 and 0.30. All of these effects suggested greater selectivity in the case of 2,4-TDI, which is also reflected by the final composition of the system (Table 9).

The reaction of 2,4-TDI and alcohol (shown below) represents the sequence which takes place in polyurethane synthesis up to about 67% reaction.

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TABLE 8. The Results of Kinetic Measurements of the Reaction between 2,4′-DBDI and *n*-Butanol in Benzene in Comparison with 2,4-TDI [3] ($mol^{-1} \cdot min^{-1} \cdot L$)[a]

No. of kinetic reaction	Isocyanate	Type[b]	°C	$(k_1 + k_2) \times 10^2$ Initial	$(k_1 + k_2) \times 10^2$ Average	k_2/k_1	k_1/k_1'	k_2/k_2'	$k_1 \times 10^{-2}$	$k_2 \times 10^{-2}$	$k_1' \times 10^{-2}$	$k_2' \times 10^{-2}$
14	2,4′-DBDI	Ac	60	1.59	1.92	8.06	0.67	1.38	0.175	1.41	0.262	1.02
15	2,4-TDI	Av	30	3.40	3.56	4.08	4.48	4.33	0.701	2.86	0.158	0.66

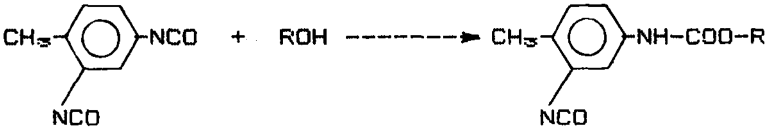
[a] Concentration = 0.175 mol/L; NCO/OH = 2.

[b] Ac = diisocyanate with constant asymmetry [3]. Av = diisocyanate with variable asymmetry [3]. k_1 = reaction rate constant in *ortho* position. k_2 = reaction rate constant in *para* position. k_1' = reaction rate constant in *ortho* position, after 2,4-TDI had been reacted in *para* position. k_2' = reaction rate constant in *para* position, after 2,4-TDI had been reacted in *ortho* position.

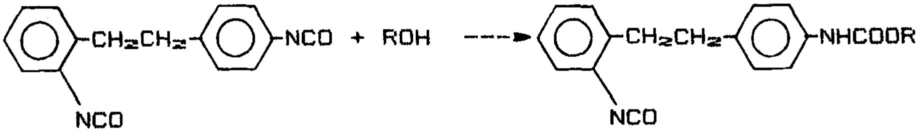
TABLE 9. Final Composition Calculated by Using a Search Method [3] Compared to Experimentally Determined Values[a]

No. of kinetic reaction	Isocyanate	n		m_1		m_2		b	
14	2,4'-DBDI	16.96	(16.5)	4.63	(5.0)	61.5	(62.0)	16.96	(16.5)
15	2,4-TDI	9.47	(10.5)	13.33	(13.0)	67.73	(66.0)	9.47	(10.5)

[a] n = unreacted diisocyanate. m_1 = *ortho* monoreacted diisocyanate. m_2 = *para* monoreacted diisocyanate. b = bireacted diisocyanate.



A similar situation exists for 2,4'-DBDI when ROH is *n*-butanol of up to about 62%.



The final composition of these systems is presented in Table 9.

CONCLUSIONS

By studying the reactivity of dibenzyldiisocyanates and comparing them with other well-known diisocyanates, it is concluded that the reactivity of 4,4'-DBDI was very similar to that of 4,4'-MDI.

In the case of 2,2'-DBDI, geometric effects were clearly evident. Reactivity is influenced by the steric effects which lead to significant intramolecular catalytic activity.

From the reactivity standpoint, 2,4'-DBDI is similar to 2,4-TDI, although the selectivity of the NCO groups at the *ortho* and *para* positions was lower than that of 2,4-TDI. The former material has important practical implications since it is a liquid with a low vapor pressure and thus reduces the risk of inhalation.

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